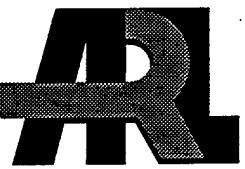


ARMY RESEARCH LABORATORY



Optical Measurement of Toxic Gases Produced During Firefighting Using Halons

by Kevin L. McNesby, Robert G. Daniel,
Andrzej W. Mizolek, and Steven H. Modiano

ARL-TR-1349

April 1997

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Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5066

ARL-TR-1349

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Optical Measurement of Toxic Gases Produced During Firefighting Using Halons

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Abstract

Several optical techniques Fourier transform infrared (FT-IR) emission and absorption spectroscopy, mid- and near-infrared tunable diode laser (MIR-TDL, NIR-TDL) absorption spectroscopy have been used to measure toxic gases produced during inhibition of flames by halogenated hydrocarbons (Halons). Fire types studied include low-pressure premixed flames, atmospheric-pressure counterflow diffusion flames, open-air JP-8 (turbine fuel) fires, and confined JP-8 fires. Spectra are presented and analyzed for these fires inhibited by CF_3Br (Halon 1301) and $\text{C}_3\text{F}_7\text{H}$ (FM-200). For low-pressure premixed flames, spectra are presented that show production of the $\text{CF}_3\cdot$ radical in $\text{CH}_4/\text{O}/\text{Ar}$ flames inhibited by CF_3Br . For real-scale fire testing, it is shown that type and amount of toxic gases produced during fire inhibition are highly dependent on fire conditions and temperatures, and that some species not considered important (CF_2O) are often produced in significant amounts. Finally, it is shown that HF production, during inhibition of vehicle fires using FM-200, is highly dependent on time to suppression.

ACKNOWLEDGMENTS

We would like to acknowledge support from Mr. Steve McCormick at U.S. Army Tank-automotive and Armaments Command (TACOM) and from the Strategic Environmental Research and Development Program (SERDP)* of the Department of Defense (DOD). We also wish to acknowledge the support of Craig Herud, Bill Bolt, and Stan Polyanski of the Aberdeen Test Center (ATC) for overseeing the running of the tests and the testing facility, and without whom these tests would have been impossible.

* The project was originally funded under the auspices of the SERDP of the DOD.

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1. INTRODUCTION

The investigations at the U.S. Army Research Laboratory (ARL) into halogenated hydrocarbon (Halon) inhibition of flames began several years ago as a project* to elucidate mechanisms of suppression using low-pressure premixed flames. This investigation was expanded to include atmospheric-pressure counterflow diffusion flames by an ongoing collaboration with the Aberdeen Test Center (ATC) to evaluate new test methods and equipment for suppression of real-scale fires occurring within the crew compartment of combat vehicles. Results of these studies have recently appeared in the literature [1, 2]. Since beginning these investigations, we have also been measuring production of toxic gases during Halon inhibition of flames.

The purpose of this report is to describe how the fire-inhibitant testing methodology in our lab has changed as our focus expanded from controlled laboratory-scale fires to real-scale fires. We also present some recent results (using laser-based diagnostics) of measurements of toxic gas production and measurements of precursors to toxic gases during Halon inhibition of laboratory-scale fires and real-scale fires in ordinary and demanding environments. To our knowledge, this is the first report of optical measurement of the $\text{CF}_3\cdot$ radical in inhibited, low-pressure premixed flames, and is the first report of quantitative, *in situ*, real-time measurements of HF gas production during large-scale firefighting by Halons.

The fire types investigated for production of toxic gases during inhibition by Halons range from controlled laboratory-scale flames to open-air JP-8 (turbine fuel) pan fires. Controlled laboratory-scale flames include low-pressure premixed $\text{CH}_4/\text{O}_2/\text{Ar}$ and CH_4/air flames and atmospheric-pressure CH_4/O_2 and CH_4/air counterflow diffusion flames [1, 2]. Real-scale fires include open-air JP-8 pan fires [3] and confined JP-8 pan fires. Gas production was measured using optical diagnostics including midinfrared tunable diode lasers (MIR-TDL), near-infrared tunable diode lasers (NIR-TDL), and Fourier transform infrared (FT-IR) emission and absorption spectroscopy. Inhibitants investigated include CF_3Br (Halon 1301 [DuPont]), $\text{C}_3\text{F}_7\text{H}$ (FM-200

* The project was originally funded under the auspices of the Strategic Environmental Research and Development Program (SERDP) of the U.S. Department of Defense (DOD).

[Great Lakes Chemical]), $C_3F_6H_2$ (FE-36), C_2F_5H (FE-25), CF_3H (FE-13), and CF_4 . For this report, only inhibition by CF_3Br (Halon 1301) and C_3F_7H (FM-200) will be discussed.

2. EXPERIMENTAL

Details of the experimental apparatus and equipment used in some of these measurements have been previously published [1, 2, 3], but will be summarized in the following sections.

2.1 Laboratory-Scale Fires.

2.1.1 Low-Pressure Premixed Flames. The experimental apparatus consisted of a low-pressure flat-flame burner (McKenna Industries, Inc.) mounted on translational stages inside an evacuable chamber. The evacuable chamber is equipped with apertured LiF windows (1.5-mm diameter) to allow passage of infrared laser radiation. Since the infrared laser beam or modulated FT-IR beam used to probe the burner flame remains fixed in position relative to the low-pressure burner chamber, different parts of the flame are examined by moving the burner within the chamber. Typical gas flow rates were 0.95 L/min CH_4 , 1.9 L/min O_2 , and 3.0 L/min Ar. Ar was used as a diluent in order to lower the peak flame temperature to the working range of Pt-Pt/Rh thermocouples (~2,000 K). Inhibitor flow was typically less than 2% of the total (fuel plus oxidizer) flow, although the low-pressure flames could withstand inhibitor Halon 1301 levels up to 15% of total flow without being extinguished. Fuel, oxidizer, and inhibitor were mixed together prior to entering the final mixing section immediately below the burner frit. Typically, an Ar shroud (3 L/min) was flowed around the flame to minimize absorption by cold gas in the line-of-sight. Gas flow was controlled by a MKS Instruments Inc., type 147B, gas flow controller. Total pressure within the burner chamber was maintained near 20 torr, although stable flames could be maintained from near atmospheric to less than 2 torr.

Midinfrared laser radiation used to probe the low-pressure premixed flames was provided by a liquid-nitrogen-cooled tunable diode laser (cryogenically cooled Pb-salt laser source and monochromator system from Laser Photonics, Analytics Division, Inc.) and detected using a

liquid-nitrogen-cooled HgCdTe narrow-band infrared detector. Laser output was frequency modulated (1 kHz), collimated, and mode selected prior to entering the low-pressure chamber. After passing through the flame region, the midinfrared laser beam was focused onto the liquid-nitrogen-cooled HgCdTe detector. Lock-in detection at the modulation frequency effectively discriminated against emission from the flame. Entrance and exit apertures mounted on the evacuable-burner chamber restricted the maximum beam diameter through the flame to 1.5 mm.

FT-IR absorption measurements through low-pressure premixed flames were made using a Mattson Sirius FT-IR spectrometer. The collimated beam from the infrared spectrometer was taken external to the instrument, apertured to 1-mm diameter, brought to a focus above the center of the burner, and then refocused onto a liquid-nitrogen-cooled HgCdTe wide-band infrared detector. FT-IR emission measurements used a Midac model G-5001-FH spectrometer system modified in-house to measure radiation emitted from the flame. Because of the modular nature of the Midac spectrometer, modification of the instrument to measure emission spectra was straightforward and consisted of repositioning the interferometer “brick” and liquid-nitrogen-cooled InSb detector to accommodate the burner flame as the source of radiation.

2.1.2 Atmospheric-Pressure Counterflow Diffusion Flames. The atmospheric-pressure counterflow diffusion burner assembly was fabricated at NIST [2], and consists of two opposing, wire-screen-covered gas ports (2.5-cm diameter). Gas port separation was adjustable, but was typically several centimeters. Fuel (CH_4) was flowed into the flame region through the lower port. Oxidizer (O_2 or air) and inhibitor were flowed into the flame region through the upper port. The flame appeared as a thin, flat luminous disc (with slight edge curvature pointing up toward the exhaust shroud) located between the fuel and oxidizer ports. All gases were exhausted from the flame region through an exhaust port that formed a shroud around the oxidizer port. Typical flow rates were 600 mL/min O_2 and 500 mL/min CH_4 . When air was used as the oxidizer, the air flow rate was 2.2 L/min and the CH_4 flow rate was 1.1 L/min. Inhibitor was always added on the oxidizer side only, and inhibitor flow varied up to a maximum of 1.3% of the total flow for each system investigated. These flow parameters were selected because they gave the most stable flame for that particular fuel/oxidizer combination.

Fuel and oxidizer flow were controlled by a MKS Instruments Inc., type 147B gas flow controller. Although the burner exhaust shroud was connected to a high-volume vacuum pump, it was necessary to contain the atmospheric-pressure counterflow diffusion burner within a large box equipped with optical ports and a chimney attached to a fume hood. This was to prevent toxic gases (HF and CF₂O) from entering the main laboratory.

2.2 Real-Scale Fires. Two types of JP-8 fuel pool fires were investigated. The first fire investigated was a JP-8 fuel pool fire burning in air. Infrared spectra of gases removed from the flame environment were measured using a Midac Corporation model G-5001-FH Fourier transform spectrometer system operating at 0.5 cm⁻¹ resolution. Detection of infrared radiation was by a liquid-nitrogen-cooled HgCdTe detector. The interior of the spectrometer was purged with dry nitrogen, and the spectrometer system was ruggedized by the manufacturer for outdoor use. This ruggedization consisted of kinematic mounting of all optical components and manufacture of all transmissive optics (including the beamsplitter) from ZnSe.

Samples of gases were removed from the flame environment and flowed through a 10-m path-length multipass optical cell (internal volume approximately 2,300 cm³) at a flow rate of 6L/min. The gas manifold and the 10-m path-length multipass optical cell contained within the instrument were maintained at 400 K to prevent condensation. The tubing leading from the stainless steel probe (0.25 in o.d. 304 stainless steel tubing) to the instrument gas manifold was of unheated teflon. No condensation was observed within the teflon tubing leading from the probe to the spectrometer, but a small amount of black soot formed on the interior surface of the teflon tubing during testing. It is assumed that measured concentrations of gases normally highly soluble in water (e.g., HF and CF₂O) were always less than actual, because of reactions of these gases with water condensed on the walls of the probe. Fires were fueled by 3 gal of JP-8 fuel placed in a 20-cm deep square pan approximately 1 m on a side. The stainless steel probe, approximately 3 m in length, was located at the edge of the pan, approximately 1 m above the surface of the liquid fuel.

Prior to ignition of the fuel (accomplished using an O₂/C₂H₂ torch), gas flow to the multipass cell was begun, a background scan set measured, and a series of sample scan sets was begun. Each scan set consisted of 10 coadded scans measured at 0.5 cm⁻¹ resolution. Collection of these scan sets continued throughout the course of the experiment. Chemical inhibitor (either Halon 1301 or FM-200) was sprayed into the fire using a hand-held extinguisher 3 min after ignition of the fuel to allow the fire to stabilize. The inhibitor (Halon 1301 or FM-200) was applied to the fire from the side opposite to the location of the probe with the inhibitor stream directed toward the lower portion of the fire.

The second type of fire investigated was a JP-8 fuel pool fire burning in the crew compartment of the ballistic hull of a Bradley Fighting Vehicle. For these tests, a 0.3 m² pan was filled to a depth of approximately 1 cm with JP-8 fuel. All doors and hatches were closed, and the fire was ignited through a small access port using an O₂/C₂H₂ torch. After approximately 15 s, the onboard fire suppression system (consisting of a bottle filled with approximately 3 kg inhibitor and pressurized with N₂ to 800 psi) was deployed. Full inhibitor release and fire extinguishment (when successful) occurred in less than 1 s.

Placed within the crew compartment of the vehicle was a GRIN-lens tipped fiber optic, emitting laser radiation at 7,665 cm⁻¹. The source of the near-infrared laser radiation was a tunable diode laser spectrometer system employing a thermoelectrically cooled InGaAsP distributed feedback laser source (Southwest Sciences, Inc). The laser radiation was detected by a room temperature InSb photodiode detector (distance from fiber optic source = 10 cm). This frequency corresponds to the frequency of the P(2) line of the first overtone of the fundamental HF vibration. The laser was scanned at 50 Hz over the spectral region of interest (approximately 0.05 cm⁻¹ on either side of 7,665 cm⁻¹) and frequency modulated at 50 kHz during each scan through the spectral region of interest. Detector output was demodulated at 100 kHz (SRS Inc. Model 850 lock-in amplifier), and digitized using an oscilloscope (Lecroy 9360). Data collection was initiated prior to ignition of the fire. Each data point corresponds to one scan over the spectral region near 7,665 cm⁻¹ and to a time resolution of 20 ms. A new data point was measured every 2 s, for the duration of the experiment.

3. RESULTS

3.1 Laboratory-Scale Fires.

3.1.1 FT-IR Spectroscopy. Initial measurements in our laboratory [1], using FT-IR spectroscopy to investigate low-pressure (20-torr) premixed CH_4/O_2 flames inhibited by up to 15% Halon 1301, showed no evidence of CF_2O formation, even though calculations indicated [4] that CF_2O should be formed in small amounts. For example, Figure 1 is an FT-IR emission spectrum of gases present 10 mm above the burner surface (spatial resolution approximately 1 mm) of a 17-torr low-pressure premixed CH_4/O_2 flame to which 3% Halon 1301 has been added. This spectrum is similar in appearance to an absorbance spectrum measured through the flame at a similar height above the burner surface [2]. Emission spectroscopy was used because experiments using absorption spectroscopy to measure combustion products in flames are often complicated by absorption of radiation by cold gas species outside of the flame zone. Although significant amounts of HF are detected near $4,000 \text{ cm}^{-1}$, there is no evidence of CF_2O gas (strongest feature near $1,900 \text{ cm}^{-1}$) at any height within the flame.

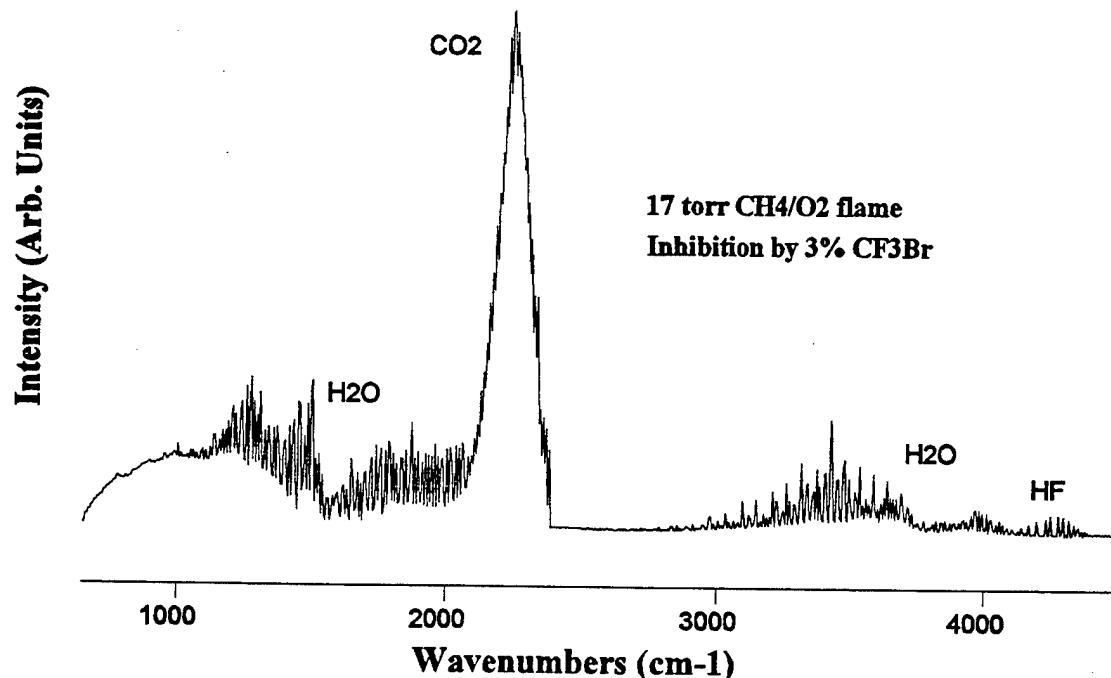


Figure 1. The FT-IR emission spectrum of gases present 10 mm above the burner surface of a 17-torr, stoichiometric, premixed gas, CH_4/O_2 flame to which 3% Halon 1301 has been added.

Figure 2 shows the FT-IR absorption spectrum measured through an atmospheric-pressure counterflow diffusion CH₄/air flame [2] inhibited by 1.3% Halon 1301. In this spectrum, formation of CF₂O gas is measured near 1,900 cm⁻¹, as well as CO (2,100 cm⁻¹), HBr (2,700 cm⁻¹), and HF (4,000 cm⁻¹). More species are observed in the atmospheric-pressure counterflow diffusion flame than in the low-pressure premixed flame because the peak temperature in the counterflow diffusion CH₄/air flame is several hundred Kelvins lower [2] than in the low-pressure CH₄/O₂ flame. Species generated in the lower temperature flame have a longer residence time than in the low-pressure CH₄/O₂ flame, allowing measurement of CF₂O and HBr in the counterflow diffusion CH₄/air flame.

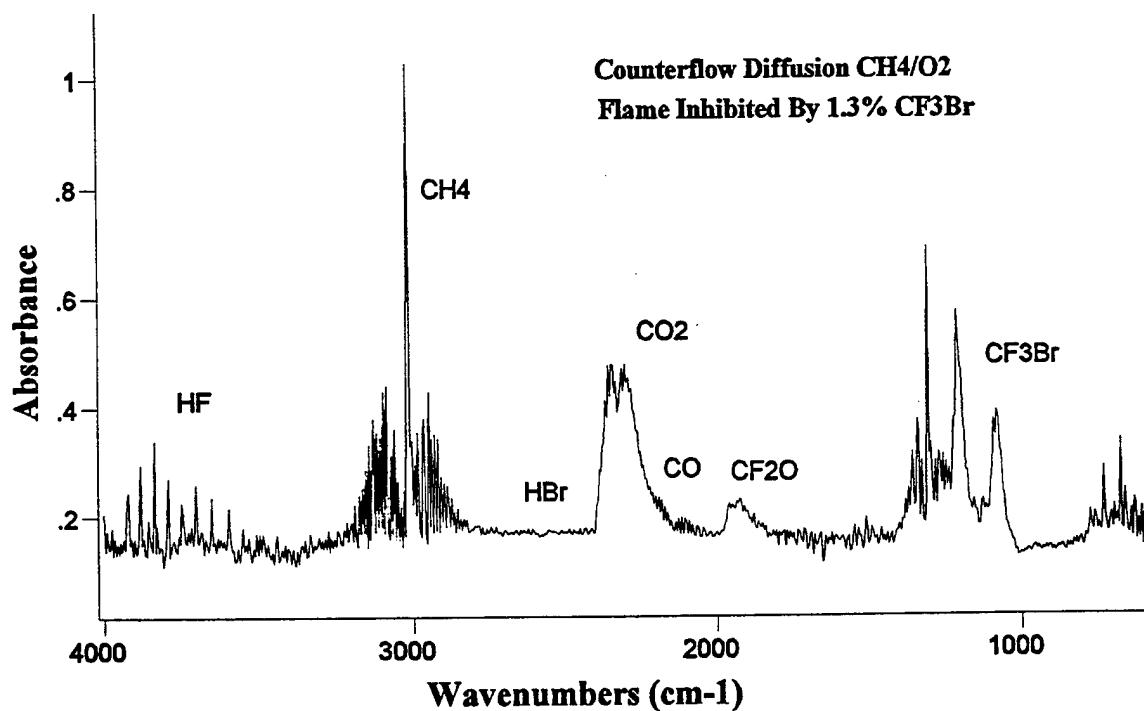


Figure 2. The FT-IR absorbance spectrum measured through an atmospheric-pressure counterflow diffusion CH₄/air flame inhibited by 1.3% Halon 1301.

These initial studies using FT-IR spectroscopy provide spectroscopic evidence that gas production during Halon inhibition of fires is highly dependent on the fire type and conditions. In our investigations aimed at validating flame modeling calculations [5], we used low-pressure

flames because at low pressure, flame zones are expanded and more information is available from optical measurements using our finite-spatial resolution (typically 1 mm). However, for measurements of some species present at low concentrations within the low-pressure flame, we were limited by the optical resolution of most commercial FT-IR spectrometers (usually on the order of 0.5 cm^{-1}).

3.1.2 Tunable Diode Laser Spectroscopy. To measure species at concentrations below the detection limit of our Fourier transform spectrometer, we employed tunable diode laser absorption spectroscopy using phase-sensitive detection. The instrumental methods employed in using such derivative-based spectroscopies have been well characterized in the literature [6]. The principle advantages of the technique are high resolution (typically better than 0.0005 cm^{-1}), increased sensitivity (because of the use of phase-sensitive detection), and (at high laser modulation frequencies) low source noise.

Figure 3 shows second-derivative MIR-TDL absorption spectra measured through rich and lean 21-torr $\text{CH}_4/\text{O}_2/\text{Ar}$ flames doped with 5% Halon 1301. These spectra were measured using a probe-beam waist of 1.5 mm, with the beam center axis 3 mm above the burner surface. The spectral region of interest was determined by the reported frequencies of $\text{CF}_3\cdot$ and CF_2O absorptions [7], by the spectral structure of the reference gas (N_2O), and by the output range of our diode laser system. The spectral region selected was from $1,264.3 \text{ cm}^{-1}$ to $1,264.7 \text{ cm}^{-1}$. In addition to encompassing several absorption lines of $\text{CF}_3\cdot$ and CF_2O , this spectral region was selected because it was free from absorptions from the reference gas (N_2O), CH_4 , Halon 1301, CO_2 , and H_2O , and because the CF_2O absorption features present in this region, although dense, were recognizable and had a weak temperature dependence as calculated using the HITRAN [8] database. Because of the low anticipated concentrations of the $\text{CF}_3\cdot$ radical, we did not consider interferences from C_2F_6 , although for higher concentrations of the $\text{CF}_3\cdot$ radical it has been shown that absorption from C_2F_6 may be important [7]. The $\text{CF}_2\cdot$ radical has no reported absorbance in this region [9]. The main experimental difficulty in detecting $\text{CF}_3\cdot$ in flames inhibited by Halons is that the spectral features from the radical are usually obliterated by the dense spectral structure of CF_2O .

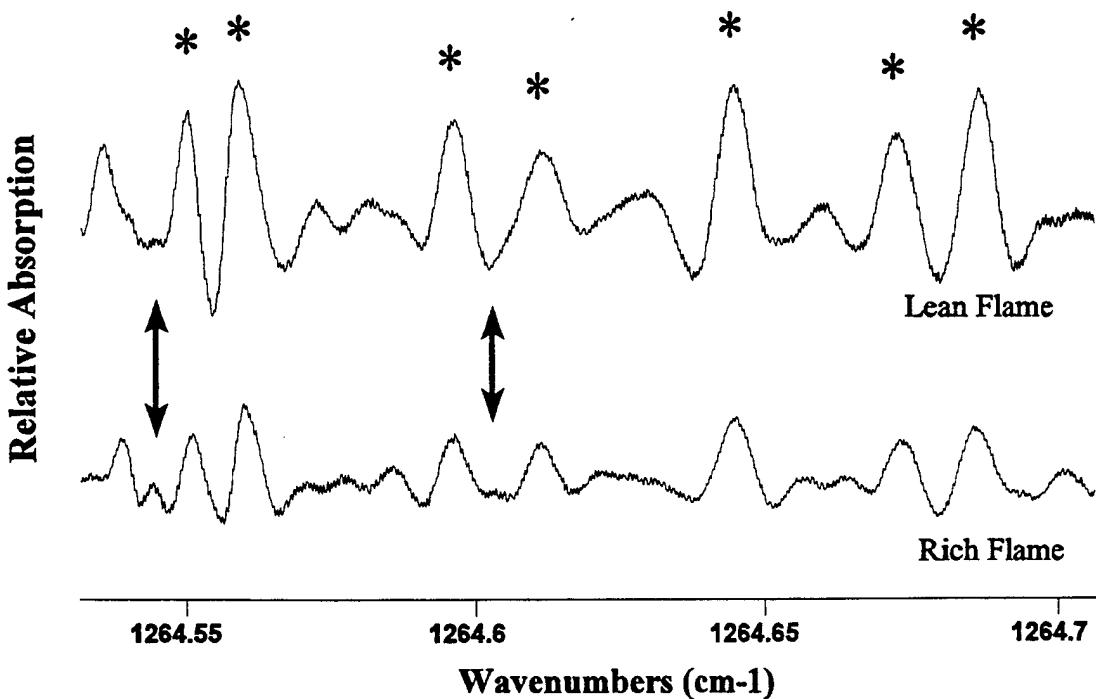


Figure 3. Second derivative MIR-TDL laser absorption spectra measured through rich and lean 21-torr premixed CH_4/O_2 flames inhibited by 5% Halon 1301. Spectra for each flame were measured 3 mm above the burner surface. The position of an absorption feature due to CF_2O is indicated by an asterisk. Double-headed arrows indicated positions of $\text{CF}_3\cdot$ absorption. Note that CF_2O absorption is greater in the lean flame, while $\text{CF}_3\cdot$ absorption is greater in the rich flame (see text).

Several features may be noted from the spectra shown in Figure 3. Most importantly, features due to absorption of radiation by CF_2O (marked with an asterisk) are seen to be more intense for the lean flame (1.9 l/m O_2 , 0.76 l/m CH_4 , 1.0 l/m Ar) than for the rich flame (1.7 l/m O_2 , 1.0 l/m CH_4 , 1.0 l/m Ar). This is because excess O_2 in the lean flame may compete with H atom for reactions with $\text{CF}_3\cdot$ radical and $\text{CF}_2\cdot$ radical, increasing CF_2O formation relative to that occurring in a rich (oxygen poor) flame [10]. We have found that comparing rich- and lean-flame infrared spectra of flames with similar levels of fluorocarbon inhibitor is a useful way of aiding the identification of lines arising from absorption of infrared radiation by CF_2O . This observation reflects the different way the inhibitor participates in rich- and lean-combustion environments, and may provide insight into controlling amounts of HF and CF_2O in combustion gases.

Figure 4 shows measurements of second-derivative spectra, over the same spectral region shown in Figure 3 through the rich, 21-torr premixed $\text{CH}_4/\text{O}_2/\text{Ar}$ flame doped with 5% Halon 1301 (and shown in Figure 3), as a function of height above the burner surface. As in Figure 3, absorption by CF_2O is indicated by asterisks. Arrows indicate the position of absorption of infrared radiation by CF_3^\cdot . For Figure 4, two features (at $1,264.557 \text{ cm}^{-1}$ and $1,264.604 \text{ cm}^{-1}$), corresponding to absorption by CF_3^\cdot , are not obscured by absorption by CF_2O . The absorption at $1,264.557 \text{ cm}^{-1}$ is more intense than the absorption at $1,264.604 \text{ cm}^{-1}$ and first appears 1 mm above the burner surface. The absorption at $1,264.557 \text{ cm}^{-1}$ disappears as height above the burner surface is increased. The smaller absorption near $1,264.604 \text{ cm}^{-1}$ appears approximately 3 mm above the burner surface, and vanishes at approximately 4 mm above the burner surface.

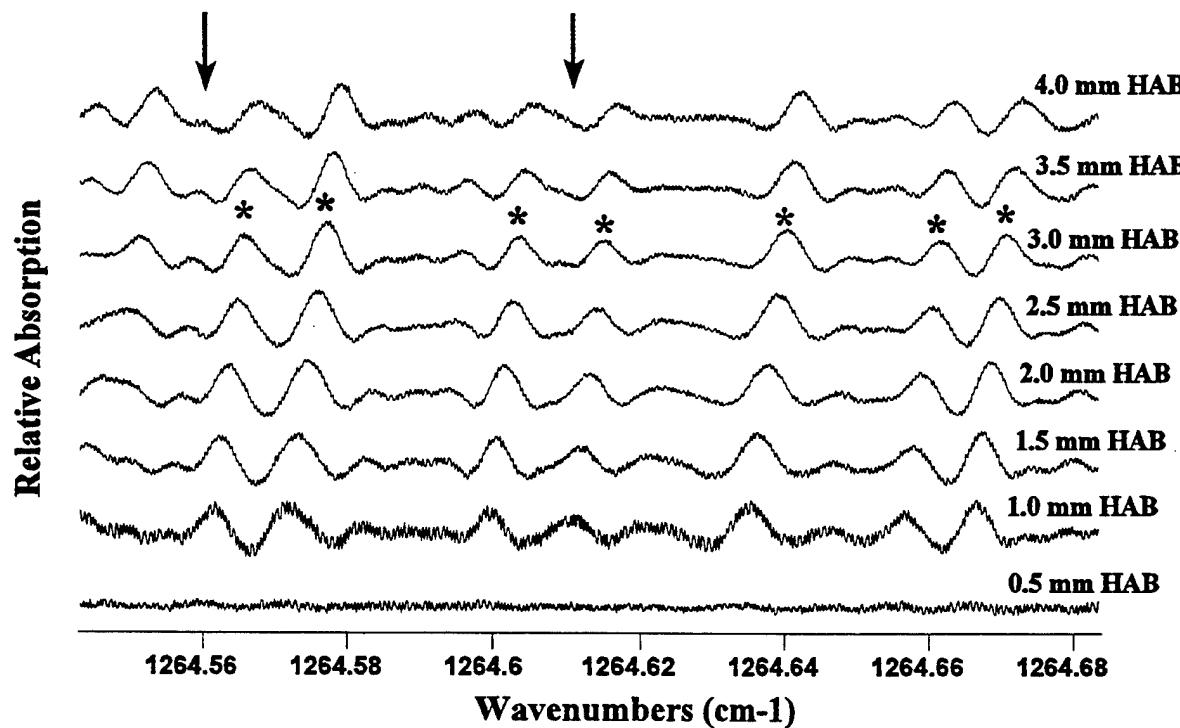


Figure 4. Second derivative MIR-TDL absorption spectra measured through a rich premixed $\text{CH}_4/\text{O}_2/\text{Ar}$ flame to which 5% Halon 1301 has been added, measured as a function of laser-beam height above burner (HAB) surface. The position of an absorption feature due to CF_2O is modeled indicated by an asterisk. Arrows indicate positions of CF_3^\cdot absorption. Note how CF_3^\cdot absorption first increases, then decreases, with increasing height above burner surface, in agreement with flame kinetics.

We believe the absorption features seen in the spectra of Halon 1301 inhibited flames at $1,264.557\text{ cm}^{-1}$ and $1,264.607\text{ cm}^{-1}$ are the first optical measurement of the $\text{CF}_3\cdot$ radical in Halon-inhibited low-pressure flames. The successive spectra show an increase, followed by a decline, with height above the burner surface, for the two features at frequencies previously assigned to the $\text{CF}_3\cdot$ radical. This spatial dependence is consistent with predictions from flame model calculations of inhibited flames [10]. The intensity of these two features, in proportion to CF_2O absorption, changes in qualitative agreement with flame modeling calculations. However, it may be seen from Figure 4 that there remain many unassigned features in each spectrum, so an unambiguous assignment of these weak features to $\text{CF}_3\cdot$ may not be made until more than two transitions have been identified.

3.2 Real-Scale Fires.

3.2.1 FT-IR Spectroscopy. Measurement of gases produced during real-scale fire testing was performed at the ATC. All fires investigated used JP-8 as fuel. JP-8 is a turbine engine fuel composed of long chain (C_n , $n > 5$) hydrocarbons. Figure 5 shows the FT-IR absorbance spectrum of gases removed from the vicinity of the fire during inhibition of the fire by Halon 1301. Evident from this spectrum are features due to HF, HCl, HBr, CO, and CF_2O , as well as other species participating in the combustion. Most noticeable is the difference between species present in this fire vs. those observed in the laboratory-scale fires. Most significant are the prominent features due to HBr and CF_2O . We believe the HCl present in the flame arises from Cl impurities in Halon 1301, although no effort was made on our part to verify impurities present in any of the inhibitants used in these experiments. The optically determined concentrations of gases present during inhibition of open-air JP-8 pan fires by Halon 1301 and FM-200 have recently been reported by us elsewhere [3].

3.2.2 Tunable Diode Laser Spectroscopy. Results from measurements using FT-IR (Figure 5) showed significant concentrations of HF and CF_2O gas produced during inhibition of open air JP-8 fuel pan fires by Halon 1301. For testing of fire inhibition by Halons in occupied areas, it is important to measure, *in situ*, the time evolution of any toxic gases produced

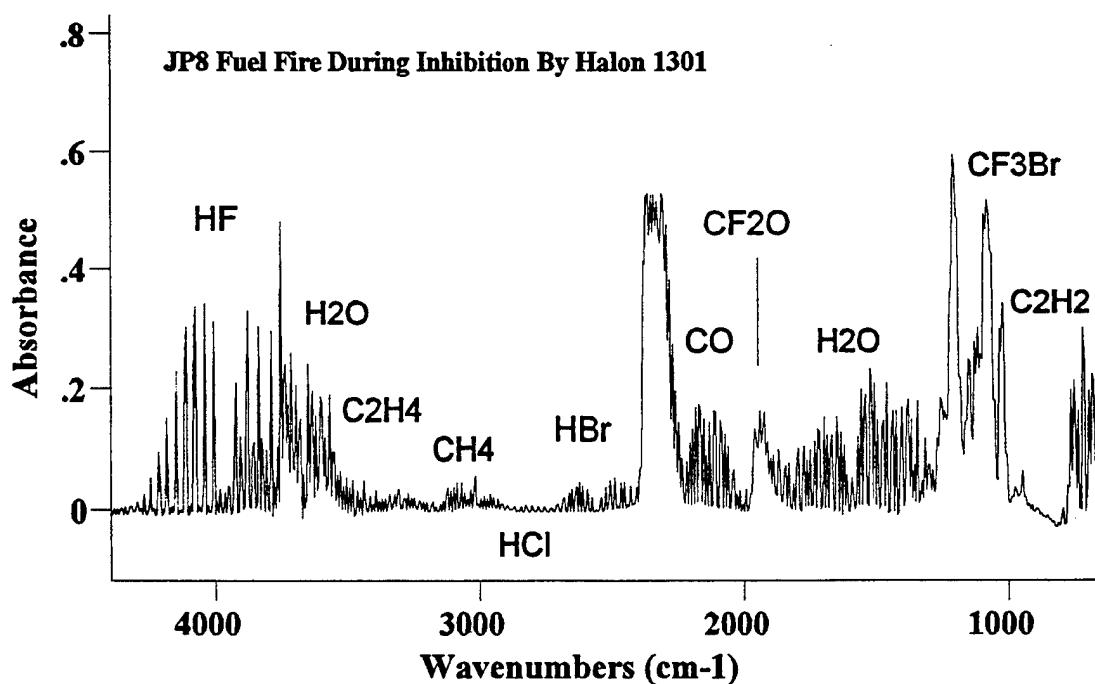


Figure 5. The FT-IR absorbance spectrum of gas removed from the vicinity of a JP-8 fuel pool fire during inhibition by Halon 1301.

during the inhibition event. This is important for measurement of HF, since we have observed that HF reacts rapidly with most surfaces, especially in the presence of moisture. For this reason, tunable diode laser spectroscopy was chosen to be one of the diagnostics employed during testing. HF was selected as the most important gas to monitor, since HF typically has the highest partial pressure of any of the Halon-inhibited-flame toxic gas products.

Figure 6 shows a schematic of the facility for measuring gases produced during suppression of JP-8 fires occurring within the crew compartment of a ballistic hull and turret of an Army combat vehicle. The HF diagnostic uses a NIR-TDL operating at $7,665\text{ cm}^{-1}$. This frequency corresponds to the frequency of the P(2) line of the first overtone of the fundamental HF vibration. There are several reasons to use diode lasers operating in the near-infrared. For HF diagnostics, however, the most important is that MIR-TDL operating at the fundamental frequency (near $4,000\text{ cm}^{-1}$) are not yet available. Other reasons for using a NIR-TDL-based

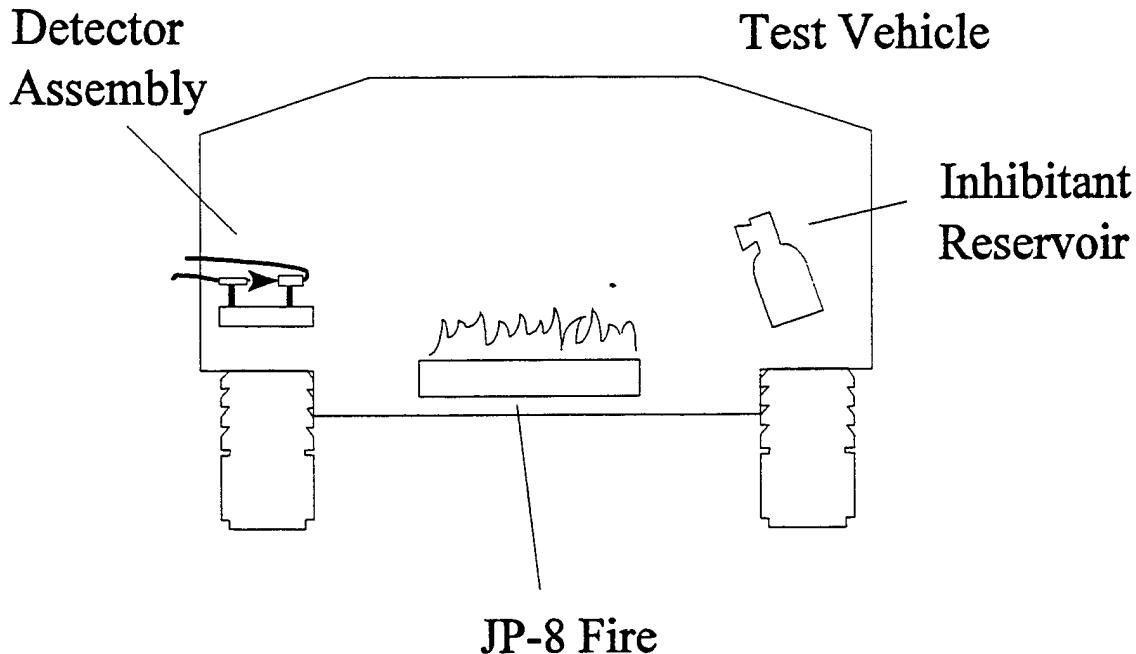


Figure 6. A schematic of the test facility for measuring gases produced during suppression of JP-8 fuel pool fires occurring within crew compartments of Army vehicles. The detector assembly consists of an extractive FT-IR probe and an in situ NIR-TDL emitter-detector assembly.

diagnostic include ease of transmission of the laser radiation through optical fibers, operation at temperatures attainable with thermoelectric coolers (~ 270 K), low cost of detectors, and ability to significantly reduce laser output noise through the use of kHz modulation techniques [11].

Figure 7 is a graph of HF gas production (in parts per million meter [ppmm]), measured using the NIR-TDL vs. time immediately after release of 3.4 kg of FM-200 into a JP-8 fuel pan fire (area ~ 0.3 m 2) burning within the closed crew compartment of the ballistic hull and turret of a Bradley Fighting Vehicle. The Halon was dispersed into the fire in approximately 1 s. Fire extinguishment occurred during dispersal of the inhibitant. Figure 8 is a graph of HF gas production (in parts per thousand meter [pptm]), measured using the NIR-TDL vs. time for an identical test, except that the fire was not extinguished by the Halon. The only difference between

HF Production - Crew Compartment

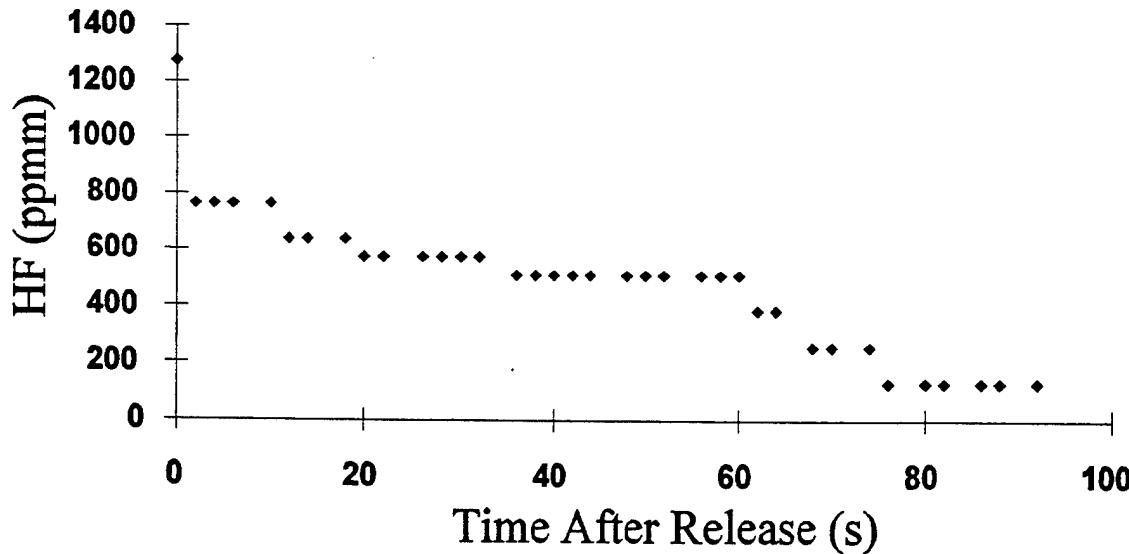


Figure 7. A graph of HF production (parts per million meter [ppmm]) vs. time after release of FM-200 for a JP-8 fuel pool fire occurring within the crew compartment of an Army combat vehicle. For this test, the inhabitant extinguished the fire.

HF Production - Crew Compartment

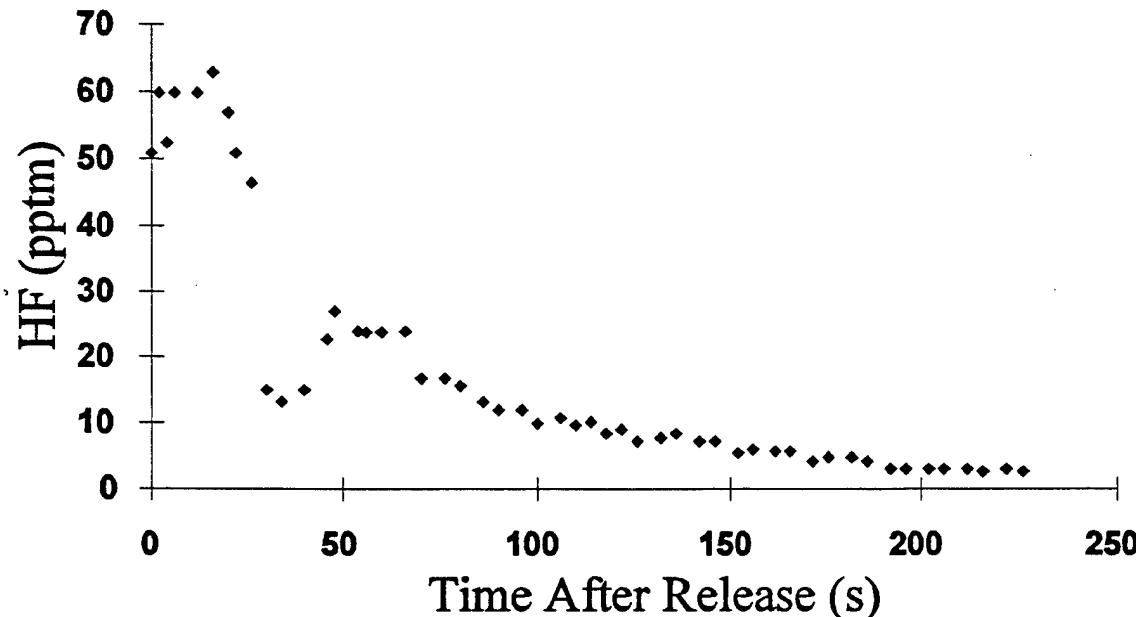


Figure 8. A graph of HF gas production (parts per thousand meter [pptm]) vs. time immediately after release of FM-200 into JP-8 fuel pool fire burning within the closed crew compartment of an Army combat vehicle. Unlike the data shown in Figure 7, for this test, the fire was not extinguished by the inhabitant. The dip in HF concentration near 40 s is due to activation of the backup CO₂ extinguisher system.

tests is a slight change in position of the nozzle of the canister from which the Halon is dispersed. From Figures 7 and 8, it may be seen that peak HF production in the fire not extinguished by the Halon is approximately 50 times higher than in the fire in which extinguishment by the Halon occurred immediately. The dip in HF concentration in Figure 8 near 40 s marks the time at which the backup CO₂ extinguishment system was used to put out the fire. These results indicate that time to suppression, when using Halon-based fire inhibitants, is a critical factor in determining amount of toxic gas (HF) produced during fire fighting. We believe these results are the first quantitative, in situ, real-time measurements of HF production during inhibition of real-scale fires using Halons.

4. CONCLUSION

Optically-based measurements can provide valuable diagnostic information necessary for determination and analysis of mechanisms and efficiencies of Halon fire inhibitants. We have shown that production of toxic gases associated with fire inhibition by Halons, particularly HF and CF₂O, is dependent on the type and conditions of the fire being investigated. We have measured differences in concentrations of CF₃[·] produced in rich and lean flames inhibited by Halon 1301. Finally, we have shown that the time evolution of HF gas produced during inhibition is dependent on whether or not fire suppression is accomplished immediately after application of Halon inhibitant. We are currently exploring the application of the diagnostic techniques mentioned in this report to more types of fires and extending the methods described here to even more extreme environmental conditions.

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	April 1997	Final, Jan 95-Jan 96	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Optical Measurement of Toxic Gases Produced During Firefighting Using Halons		PR: 1L161102AH43	
6. AUTHOR(S)			
Kevin L. McNesby, Robert G. Daniel, Andrzej W. Mizolek, and Steven H. Modiano			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION REPORT NUMBER	
U.S. Army Research Laboratory ATTN: AMSRL-WM-PC Aberdeen Proving Ground, MD 21005-5066		ARL-TR-1349	
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Approved for public release; distribution is unlimited.			
13. ABSTRACT (Maximum 200 words)			
<p>Several optical techniques Fourier transform infrared (FT-IR) emission and absorption spectroscopy, mid-and near-infrared tunable diode laser (MIR-TDL, NIR-TDL) absorption spectroscopy have been used to measure toxic gases produced during inhibition of flames by halogenated hydrocarbons (Halons). Fire types studied include low-pressure premixed flames, atmospheric-pressure counterflow diffusion flames, open-air JP-8 (turbine fuel) fires, and confined JP-8 fires. Spectra are presented and analyzed for these fires inhibited by CF₃Br (Halon 1301) and C₃F₇H (FM-200). For low-pressure premixed flames, spectra are presented that show production of the CF₃[·] radical in CH₄/O/Ar flames inhibited by CF₃Br. For real-scale fire testing, it is shown that type and amount of toxic gases produced during fire inhibition are highly dependent on fire conditions and temperatures, and that some species not considered important (CF₂O) are often produced in significant amounts. Finally, it is shown that HF production, during inhibition of vehicle fires using FM-200, is highly dependent on time to suppression.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Halons, toxic gas generation, hydrogen fluoride		37	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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